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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON SOME REGULARITIES IN THE VIBRATIONAL SPECTRA OF ORGANOSILICON COMPOUNDS

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The paper presents the results of a study of the vibrational spectra of organosilicon compounds of the type $Cl_n(CH_3)_{3-n}SiCH=CH_2$; $Cl_n(CH_3)_{3-n}SiCH_2$—$CH=CH_2$ (I) (the constants of these compounds are given in Table 1); $(CH_3)_3Si(CH_2)_n$—$CH=CH_2$ (II) ($n = 0 \div 3$), as well as compounds $(CH_3)_3ECH_2$—$CH=CH_2$ ($E = C, Si, Ge, Sn$).

The infrared absorption spectra were recorded on infrared spectrometers:
1) on a double-beam spectrophotometer based on a VIKS M-3 spectrometer with pris-

Fig. 1. Infrared absorption spectra of compounds of the series
$Cl_n(CH_3)_{3-n}SiCH=CH_2$
($n = 0$—3)

NaCl; 2) on the same instrument with a LiF prism; 3) on an IKS-12 single-beam infrared spectrometer with a KBr prism. The molar absorption coefficients of the C=C bonds were determined for solutions in octane.

For recording the substances, cells with a layer thickness of 0.050 mm with NaCl windows and 0.016 mm with KBr windows were used. Raman spectra were recorded on an ISP-51 spectrograph with registration on FEhP-1. The intensities in the Raman spectra were estimated relative to the 458 cm^{-1} line in CCl_4, whose intensity was taken as 100.

Fig. 2. Infrared absorption spectra of compounds of the series

$$Cl_n(CH_3)_{3-n}SiCH_2-CH=CH_2 \quad (n = 0\text{—}3)$$

1. It turned out that, for the series $Cl_n(CH_3)_{3-n}SiCH = CH_2$, the intensity of the absorption bands of the C=C bond ($\nu_{C=C} = 1600$ cm^{-1}) increases strongly as n increases (the optical density increases threefold); whereas for the series $Cl_n(CH_3)_{3-n}SiCH_2 - CH = CH_2$ ($\nu_{C=C} = 1635$ cm^{-1}) the opposite regularity is observed (Figs. 1, 2, 3).

The different nature of the trimethyl- and trichlorosilyl groups is manifested not only in the vibrational spectra, but also in the chemical behavior of compounds containing these groupings. This may include the results of studies of addition reactions at the double bond of halogens and hydrogen halides for the series $Cl_n(CH_3)_{3-n}SiCH_2 - CH = CH_2$, indicating differences in the behavior of the end members of this series in a number of cases ([1]); moreover, the order of addition of HBr to the C=C bond under certain reaction conditions for $(CH_3)_3SiCH_2 - CH = CH_2$ and $Cl_3SiCH_2 - CH = CH_2$ is completely opposite ([1-3]) (this concerns Markovnikov' s rule).

There are also data on the different interaction of the terminal members of the series $Cl_n(CH_3)_{3-n}SiCH = CH_2$ and $Cl_n(CH_3)_{3-n}SiCH_2—CH = CH_2$ with silicon chloroform ($HSiCl_3$) (4), which agrees with the quite appreciable difference in the course of the intensities* for the absorption bands of the C = C bonds of the compounds of each of these series (Fig. 3). Such a difference in the course of the intensities is associated with the different character of the C = C bonds (vinyl and allyl), caused by the different type of their interaction with other bonds.

In the Raman spectra, the differences in the intensities of the C = C-bond lines of the terminal members of each of the series are either not very sharp (in the case of $Cl_n(CH_3)_{3-n}SiCH = CH_2$), or lie within the limits of accuracy of their measurement (for $Cl_n(CH_3)_{3-n}SiCH_2—CH = CH_2$).

2. The difference in the character of double bonds as a function of their distance from the silicon atom can be seen from the example of the series of compounds $(CH_3)_3Si(CH_2)_nCH = CH_2$ ($n = 0—3$) (II). From Fig. 4 it is seen that the absorption band of the allyl C = C bond is the most intense, and the vinyl one the least intense; for the γ-position the intensity is less than for the β (allyl) position, and for δ a certain increase in intensity is observed in comparison with γ (for the α-, β-, γ- and δ-positions the intensities in the Raman spectra are respectively 20, 46, 23, 25 units).

The IR-band and Raman-line frequencies increase somewhat with increasing n in series II, approaching the frequency values for an isolated double bond in olefins (the half-widths of the IR absorption bands of the C = C bonds are practically the same).

Fig. 3. Dependence of the optical densities of the absorption bands of C = C bonds for vinylmethylchlorosilanes (1) and allylmethylchlorosilanes (2) on the number of chlorine atoms at Si.

The fact of alternation of the intensities of Raman lines and IR absorption bands

Fig. 3. Dependence of the optical densities of the absorption bands of C = C bonds for vinylmethylchlorosilanes (1) and allylmethylchlorosilanes (2) on the number of chlorine atoms at Si

Figure 2: Fig. 3. Dependence of the optical densities of the absorption bands of C = C bonds for vinylmethylchlorosilanes (1) and allylmethylchlorosilanes (2) on the number of chlorine atoms at Si

of C = C bonds beyond the β-position was noted earlier (5). However, in our work the estimate of the intensities for $(CH_3)_3Si(CH_2)_3CH = CH_2$ (δ-position, C = C bonds) was made for the first time, which gives grounds for considering the measurement results more rigorous.

Table 1

Constants of compounds of the type $Cl_n(CH_3)_{3-n}SiCH = CH_2$ and $Cl_n(CH_3)_{3-n}SiCH_2—CH = CH_2$

Substance	B.p., °C (mm)	n_D^{20}	d_4^{20}
$(CH_3)_3SiCH = CH_2$	54.6 (744)	1.3910	0.6903
$Cl(CH_3)_2SiCH = CH_2$	82 (760)	1.4141	0.8744
$Cl_2(CH_3)SiCH = CH_2$	91 (742)	1.4270	1.0868
$Cl_3SiCH = CH_2$	92.5 (750)	1.4349	1.2335
$(CH_3)_3SiCH_2—CH = CH_2$	85.4 (752)	1.4075	0.7195
$Cl(CH_3)_2SiCH_2—CH = CH_2$	110 (758)	1.4295	0.8964
$Cl_2(CH_3)SiCH_2—CH = CH_2$	116 (735)	1.4409	1.0667
$Cl_3SiCH_2—CH = CH_2$	116.5 (750)	1.4445	1.2224

3. For the series $(CH_3)_3ECH_2—CH = CH_2$ ($E = C, Si, Ge, Sn$), on going from trimethylallylmethane to trimethylallylstannane there is observed an increas— tion of the intensity of the absorption band of the C=C bond (Fig. 4) (the

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* The estimate of intensities from optical densities, generally speaking, is not rigorous. It would have been more rigorous to measure the intensities of the C = C-bond bands of methylchlorovinyl- and methylchloroallylsilanes in solutions of definite molarity or concentration, but the preparation of such solutions could introduce additional errors owing to hydrolysis of the chlorosilanes.

Fig. 4. Changes in the absorption coefficient k_m of the bands of C=C bonds. 1 –for structures of the type $(CH_3)_3ECH_2$—$CH = CH_2$ as a function of $E = C, Si, Ge, Sn$; 2 –for structures of the type $(CH_3)_3Si(CH_2)_nCH = CH_2$ as a function of the position of the multiple bond relative to Si

Figure 3: Fig. 4. Changes in the absorption coefficient k_m of the bands of C=C bonds. 1 –for structures of the type $(CH_3)_3ECH_2$—$CH = CH_2$ as a function of $E = C, Si, Ge, Sn$; 2 –for structures of the type $(CH_3)_3Si(CH_2)_nCH = CH_2$ as a function of the position of the multiple bond relative to Si

half-width of the bands is the same and is equal to 25 cm^{-1}). At the same time, the frequency also shifts from 1650 to 1628 cm^{-1}. All this can be associated with an enhancement of the effect leading to a change in the dipole moments of the E–C and C=C bonds in the compounds $(CH_3)_3ECH_2$—$CH = CH_2$ along the series $E = C, Si, Ge, Sn$, caused by the different nature of the C atom on the one hand and Si, Ge, Sn on the other (from Fig. 4 it is seen that the dipole moment of the C=C bond increases along the series $E = C, (Si, Ge), Sn$, since it is known that $k_\nu \sim (dp/dQ_l)^2$, where p is the dipole moment).

Fig. 4. Changes in the absorption coefficient k_m of the bands of C=C bonds. **1** –for structures of the type $(CH_3)_3ECH_2$—$CH = CH_2$ as a function of $E = C, Si, Ge, Sn$; **2** –for structures of the type $(CH_3)_3Si(CH_2)_nCH = CH_2$ as a function of the position of the multiple bond relative to Si.

As for the series $(CH_3)_3ECH = CH_2$, we did not carry out special measurements of the intensities of the infrared absorption bands of the C=C bonds, but even purely qualitative observations show that the intensity of these bands decreases appreciably along the series $E = C, Si, Ge, Sn$.

The conclusion suggests itself that the elements Si, Ge, Sn differ less from one another than from C. In this connection it is worth mentioning a circumstance to which some authors previously drew attention ([6,7]), namely that Si has unfilled 3*d*-orbitals in its shell, which C does not have. In our opinion, the same considerations may be applied to Ge and Sn.

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Note: Figure translations are in progress. See original paper for figures.